

# PREPARATION OF ACTIVATED CARBONS WITH MESOPORES BY USE OF ORGANOMETALLICS

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## INTRODUCTION

Activated carbons are commercially produced by steam or  $\text{CO}_2$  activation of coal, coconut shell and so on. In general the carbons obtained give pores with a broad range of distribution. Recently, Matsumura[1] and Jagtoyen et al.[2] have reported that chemical activation with KOH or  $\text{H}_2\text{PO}_3$  provides microporous carbons with high surface area. These activated carbons are suitable for separation of molecules with small size i.e., removal of pollutant gases from exhausted substances. For applications to adsorption of macromolecules in a liquid media, however, it is important to prepare activated carbons having meso- or macropores.

Tamai et al. have found that steam activation of coal tar pitch homogeneously mixed with rare earth metal complexes brings about mesoporous carbons[3]. Also, the carbons thus obtained were confirmed to be very effective to selective adsorption of giant molecules such as humic acids and dextrans.

This study aims to provide mesoporous activated carbons from coals by use of various organometallic compounds. The carbons prepared are characterized by nitrogen adsorption to evaluate the pore size, and the crystal forms and size of metal compounds on the carbons are investigated by means of X-ray diffraction and transmission electron microscopy. The formation mechanism of the mesopores is also discussed on the basis of the results.

## EXPERIMENTAL

Three kinds of coals different in rank, i.e., Miike, Taiheiyō and Morwell coals were used for this study. The analytical data of the coals are summarized in Table 1. Each coal with particle size of minus 100 mesh was dispersed in tetrahydrofuran (THF) in Ar atmosphere. Al, Y, Ti, or Zr acetylacetonate ( $\text{Al}(\text{acac})_3$ ,  $\text{Y}(\text{acac})_3$ ,  $\text{TiO}(\text{acac})_2$ ,  $\text{Zr}(\text{acac})_4$ ) solution of THF was added to the coal dispersion and the mixture was stirred at room temperature for 1h under Ar gas. Thereafter, THF solvent was removed from the mixture by flash distillation under vacuum at room temperature and then  $100^\circ\text{C}$ . The weight percent of each metal added to the coal was adjusted to 2.5wt% before activation. Steam activation was carried out at  $900^\circ\text{C}$  for various times (3~25min).

Nitrogen adsorption isotherms at 77K were obtained by Quantachrome Autosorb-6. The X-ray diffraction measurement and transmission electron microscopic observation were performed using Rigaku RU-300 with a  $\text{CuK}\alpha$  radiation and Philips CM30 equipments, respectively.

## RESULTS AND DISCUSSION

Surface area and mesopore ratio. Figure 1 shows the change in BET surface area of various activated carbons obtained from Miike coal against activation time at  $900^\circ\text{C}$ . The data of the carbons from the coal alone are also added for comparison in this figure. When  $\text{Al}(\text{acac})_3$  was loaded on the coal and activated, the surface area increases with the time. On the other hand, the coal containing  $\text{TiO}(\text{acac})_2$  results in the carbon with an approximately constant surface area (ca.  $500\text{m}^2/\text{g}$ ) over these activation times. The pore size distribution and mesopore (2~50nm) area of each sample were obtained from nitrogen desorption by using BJH method[4]. Mesopore

ratio is given by dividing the mesopore area by the BET one. The ratios obtained were plotted against activation time (Fig. 2). The result shows that the mesopore ratios in the carbons increase with activation time. It is noteworthy that addition of the Ti chelate enhances mesopore ratio. The similar behavior was observed in the case of Taiheiyo and Morwell coal. The results are summarized in Table 2 and 3. The  $\text{TiO}(\text{acac})_2$  compound promotes to develop mesopores also in both cases and, especially in the activated carbons from Taiheiyo coal ca. 90% of total pores are consisted of mesopore structures, as can be seen in Table 2. Brown coals such as Morwell easily produce micropore structures with heat-treatment. Therefore, the mesopore ratio of the activated carbons from Morwell coal with or without metal is not so high compared with those from other coals, but it is obvious that the Ti complex contributes to the development of mesopore.

**X-ray diffraction and TEM observation.** As described above, it was found that  $\text{TiO}(\text{acac})_2$  dispersed on coals enhances the formation of mesopores. In order to understand the formation mechanism of these carbons, it is necessary to examine the form and size of Ti compounds on the activated carbons. Thus, the species of the compounds on the carbons were determined by X-ray diffraction. A profile of the carbon from Taiheiyo coal with  $\text{TiO}(\text{acac})_2$  is given in Fig. 3, together with that from the coal without metal. Several strong peaks due to metal compounds in Taiheiyo coal which contains a high amount of ash (Table 1) appear in Fig. 3(a). When  $\text{TiO}(\text{acac})_2$  loaded on the coal was activated with steam, the chelate is considered to decompose and form the cluster of the Ti oxides. The  $\text{TiO}_2$  crystals with rutile and brucite structures can be evidently identified from the lattice constants of the profile indicated in Fig. 3(b). The same results were obtained in the case of Miike and Morwell coal.

The transmission electron photomicrographs of the activated carbons from Taiheiyo coal are shown in Fig. 4. Whereas a typical amorphous structure due to carbon layers was observed in the activated carbon from the coal alone, there are some voids and  $\text{TiO}_2$  crystals with the size of few nm in the carbon with the metal (Fig. 4(b)) and at the same time these are closely present each other. Such a morphology was seen also in the carbons from the other coals. The particle size distribution of the crystals was estimated by an image analyzing technique (Fig. 5). Although the distribution is somewhat different in coal rank, most of the particles are ranging from 2 to 12 nm in diameter. Taking into account that the size of the mesopores in the activated carbons is comparable to that of  $\text{TiO}_2$  crystals, the behaviors of the metal oxides, such as migration or lacking may cause the generation of these mesopores.

## CONCLUSION

Mesoporous carbons were prepared by steam activation of metal acetylacetonates dispersed on Miike, Taiheiyo and Morwell coal. The  $\text{TiO}(\text{acac})_2$  complex was effective for the occurrence of these carbons. The surface areas and mesopore ratios were evaluated by analyzing the nitrogen adsorption isotherms. In addition, the size distribution of  $\text{TiO}_2$  crystals present on the carbons was examined by transmission electron microscopic observation. As a result it was found that the development of the mesopores is associated with the formation of  $\text{TiO}_2$  crystals on the carbons.

## REFERENCES

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Table 1 Analysis of coals

Coal	C	H	N	S + O(diff)	Ash
	(wt%, daf)			(wt%, dry)	
Miike	83.8	6.8	1.0	8.5	8.7
Taiheiyo	75.7	6.3	1.3	16.7	14.2
Morwell	65.0	4.8	0.6	29.5	1.6

Table 2 Pore characteristics of activated carbons(AC) from metal/Taiheiyo coal

Sample	Time *	Yield (%)	BET	Mesopore	Mesopore	Average pore size (nm)
			surface area (m <sup>2</sup> /g)	surface area (m <sup>2</sup> /g)	ratio (%)	
Blank/AC	6	16.3	134	72	54.0	6.24
Y(acac) <sub>3</sub> /AC	6	16.9	70	50	71.8	10.39
Al(acac) <sub>3</sub> /AC	6	20.6	347	112	32.3	3.84
TiO(acac) <sub>2</sub> /AC	6	20.9	174	156	89.7	7.06
Zr(acac) <sub>4</sub> /AC	6	18.8	163	80	48.9	5.15

\* at 900°C

Table 3 Pore characteristics of activated carbons(AC) from metal/Morwell coal

Sample	Time *	Yield (%)	BET	Mesopore	Mesopore	Average pore size (nm)
			surface area (m <sup>2</sup> /g)	surface area (m <sup>2</sup> /g)	ratio (%)	
Blank/AC	3	20.8	888	269	30.3	3.72
Y(acac) <sub>3</sub> /AC	6	14.0	729	186	25.5	3.73
Al(acac) <sub>3</sub> /AC	6	20.9	791	162	20.5	3.24
TiO(acac) <sub>2</sub> /AC	6	15.6	806	431	53.6	4.73
Zr(acac) <sub>4</sub> /AC	3	24.5	794	118	14.9	2.99

\* at 900°C

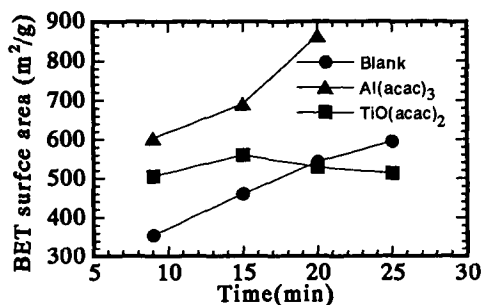


Fig. 1 BET surface area of activated carbon from metal/Miike coal

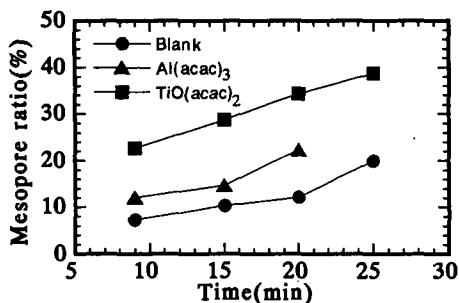


Fig. 2 Mesopore ratio of activated carbons from metal/Miike coal

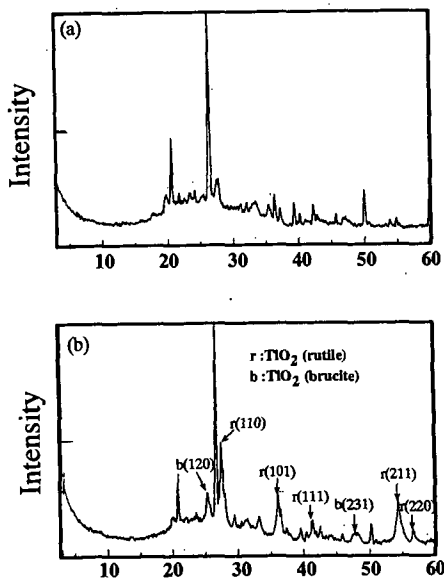


Fig. 3 X-ray diffraction profiles of AC from (a) Taiheiyo coal and (b) Taiheiyo coal/TiO(acac)<sub>2</sub>

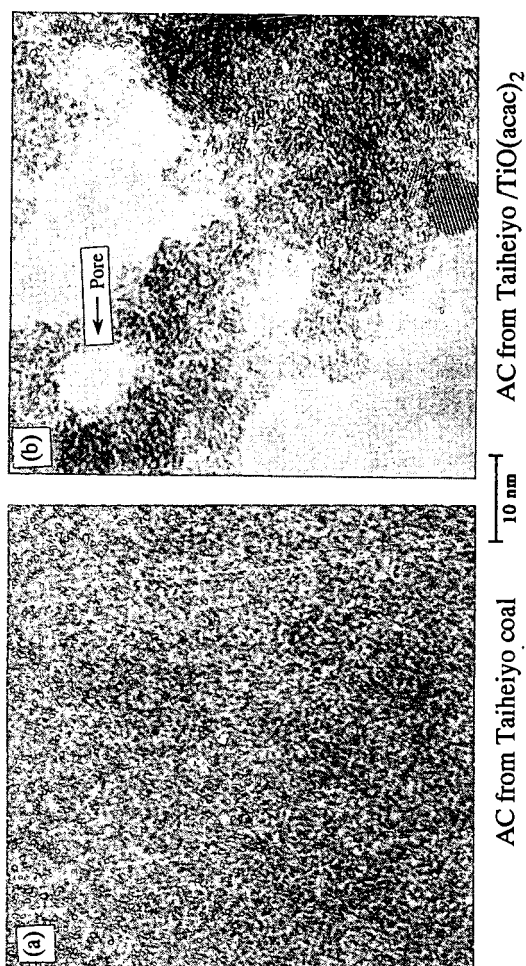


Fig. 4 Transmission electron photomicrographs of AC from  
(a) Taiheiyo coal and (b) Taiheiyo coal/TiO(acac)<sub>2</sub>

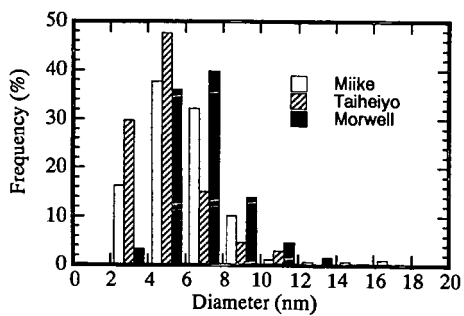


Fig. 5 Histogram of particle size of TiO<sub>2</sub> on  
activated carbon from coal/TiO(acac)<sub>2</sub>